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54 Catalyst for fischer-tropsch process.

57 A copper promoted cobalt-manganese spinel is disclosed, which is useful as a catalyst for Fischer-Tropsch synthesis of olefins and higher paraffins.

Methane is available in large quantities in many areas of the world. Some methane is generated from refinery applications while large amounts of methane, as the principal constituent of natural gas, are found in deposits in various areas.

Methane can be used directly as a gas for heating purposes and the like when the source of methane is relatively close to the end user. However, if the methane must be transported over long distances, the methane is preferably transported as a liquid.

Methane is also used as a starting material for the production of hydrocarbons. The conversion of methane is normally carried out in a two-step procedure involving reforming the methane to produce hydrogen and carbon monoxide, so-called synthesis gas or syngas, and then converting the syngas to higher hydrocarbons in a Fischer-Tropsch type reaction. Both steps of the process are well-known; for example, the first step in United States Patent Nos. 1,711,036, 1,960,912 and 3,138,438 and the second step in United States Patent nos. 4,477,595, 4,542,122 and 4,088,671.

The present invention is primarily concerned with the second step, the well-known hydrocarbon synthesis or Fischer-Tropsch reaction. To this end, the present invention provides an improved catalyst for selectively converting syngas to hydrocarbons.

The present invention provides a composition of matter comprising a copper promoted cobalt-manganese spinel, the spinel having the formula:



where x is from about 0.5 to about 1.2.

The composition is suitable for use as a Fischer-Tropsch catalyst and has the advantage that it has a high active surface area and exhibits superior performance towards the selective production of olefins and higher paraffins from synthesis gas compared with previously reported bulk or supported cobalt catalysts. Furthermore, the catalyst can be readily activated in situ, thereby avoiding complex and tedious ex situ activation schemes.

The invention also provides a method for the preparation of the cobalt-manganese spinel and the copper promoted cobalt-manganese composition. This method comprises:

- (a) forming an aqueous solution of cobalt and manganese salts of at least one alpha-hydroxy aliphatic carboxylic acid, the molar ratio of cobalt to manganese, based on the free metals, being at least 1.5:1;
- (b) evaporating the aqueous solution to yield a cobalt-manganese containing residue;
- (c) calcining the residue at elevated temperature for a time sufficient to produce the cobalt-manganese spinel of the above formula.

It has been found that by forming the cobalt-manganese mixed metal in an acid aqueous solution containing one or more alpha-hydroxy carboxylic acids, rather than the conventional aqueous alkaline solution, an improved spinel can be obtained which is a single phase spinel with a high BET (Brunauer, Emmett and Teller) surface area of at least 5 m²/g.

If the spinel is to be copper promoted, in order to form the composition of the invention, this is carried out after the calcining step using methods well-known in the art.

The composition of matter according to the invention is a copper promoted cobalt-manganese spinel, the spinel having the formula $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ where x is from about 0.5 to about 1.2, preferably from about 0.7 to about 1.0, most preferably about 1.0. Thus the ratio of cobalt to manganese in the spinel is between about 1.5:1 and about 5:1. The spinel is preferably a homogeneous, single phase spinel that is substantially isostructural with Co_3O_4 as determined by X-ray diffraction analysis.

The spinel advantageously has a high BET surface area of above 5 m²/g, preferably above 30 m²/g. Normally the surface area is in the range from about 5 to about 200 m²/g, more preferably from about 25 or 30 to about 200 m²/g, and most preferably from about 60 to 150 m²/g.

The amount of copper promoter in the composition is preferably from about 0.1 to about 5 gram atom percent based on the total gram atoms of cobalt and manganese of the dry composition, more preferably from about 0.5 to about 2.0 weight percent.

The cobalt-manganese spinel may be prepared by any suitable process for preparing spinels, these processes being well-known in the art. For example, water soluble salts of cobalt and manganese can be reacted together in an aqueous alkaline solution made alkaline, for example, by the addition of a Group I or II metal hydroxide or ammonium hydroxide.

However, it has been found that an improved spinel with the desired high surface area and a substantially homogeneous single phase can be obtained by forming an acidic aqueous solution of cobalt and manganese salts of at least one alpha-hydroxy carboxylic acid.

To perform this process, as a first step it is preferred to dissolve water-soluble salts of cobalt and manganese, for example their nitrates, sulfates, chlorides, acetates and the like in water. The concentration of the salts in the aqueous liquid is not critical to the extent that the salts are present in less than a saturated solution

to avoid precipitation. For example, an 80 to 90 percent saturated solution, of combined dissolved metal molarities for avoiding precipitation in the process, can be effectively used.

The temperature of the solution is also not critical and may be above room temperature to aid in the solubilizing process; however, room temperature is generally adequate. Further, the pressure is not critical to the process and atmospheric pressure is generally used.

The aqueous solution can also contain minor amounts of an organic solvent or solvents, such as ethanol, acetone, ethylene glycol and the like for aiding in the solubilizing of the cobalt and manganese salts.

Following the dissolving of the cobalt and manganese salts, the alpha-hydroxy acid(s) is added to the solution. This acid may contain one or more hydroxy groups and one or more carboxylic groups. Examples of suitable acids include citric, glycolic, malic, glyceric, mandelic, tartaric, and lactic acids, and mixtures thereof. Preferred carboxylic acids are citric acid and glycolic acid. The molar ratio of cobalt salt to manganese salt is at least 1.5:1, preferably between 1.5:1 and 5:1, more preferably between 2:1 and 3:1.

The amount of carboxylic acid added to the solution is beneficially at least a stoichiometric amount, i.e., a 1:1 molar ratio of metal to acid. Preferably the acid is present in a slight molar excess, for example 5 to 10% molar excess. Higher levels can be used although this is likely to be uneconomical. Lower amounts may also be used, but this would result in incomplete cobalt and manganese acid salt formation.

The pH of the solution is preferably slightly acidic, typically pH of between about 5 and about 7. To maintain this pH a base may be added to the solution, for example ammonium hydroxide, sodium hydroxide or potassium hydroxide, preferably ammonium hydroxide. The addition of the base has the advantage that it helps to solubilize the carboxylic acid salts.

The exact sequence of steps described above need not be adhered to with the proviso that the final aqueous solution contains dissolved cobalt and manganese salts of at least one alpha-hydroxy carboxylic acid. If any insoluble materials are present after the addition of the acid and any base, then these should be removed by filtering prior to the evaporation step.

The solution is then evaporated, for example by air drying or under reduced pressure, at elevated temperature, as may be practised in a rotary evaporator or in a vacuum drying area. The resulting material is a cobalt-manganese amorphous solid residue, generally in the form of a powder. Optionally, the residue can be washed with distilled water and dried, for example in vacuo at about 110°C.

The residue is then calcined by heating it in air at a temperature generally in the range of 100°C to 500°C, preferably 250°C to 350°C for sufficient time, generally between 1 and 24 hours, to yield a single spinel phase of the said formula $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ which is substantially isostructural with Co_3O_4 as determined by X-ray diffraction analysis.

The promoting of the spinel with copper, and, if desired, an additional promoter metal or metals, may be achieved by any suitable means as are known to those skilled in the art. Promotion of the spinel may be conducted by incipient wetness impregnation or multiple impregnation with one or more promoter metal salt solutions, for example copper nitrate hexahydrate.

Prior to being employed as a Fischer-Tropsch catalyst, the copper promoted cobalt-manganese spinel is reduced by exposing the composition to a reducing atmosphere at an elevated temperature. Preferably, the temperature ranges from about 240°C to about 500°C, most preferably from about 300°C to about 400°C. The reduction can be carried out with various reducing gases including hydrogen, hydrogen/carbon monoxide, and the like and mixtures thereof. Preferably hydrogen gas alone is generally used in an inert carrier medium such as helium, neon, argon, or nitrogen, in the absence of carbon monoxide when substantially pure, non-carbided catalyst is desired.

The reduction may be carried out ex situ in a tube reactor, but advantageously is carried out in situ in the Fischer-Tropsch slurry process. The in situ preparation is conducted in the slurry apparatus when the above described product is reduced while suspended in the slurry liquid. Reduction takes place in a reducing atmosphere, preferably a hydrogen/carbon monoxide-containing atmosphere, at elevated temperatures of about 200°C, or above, preferably at 230°C-300°C at a space velocity, pressure and hydrogen concentration sufficient to cause substantial reduction of the catalyst.

Although a fixed bed process can be used, a preferred process mode for operating the Fischer-Tropsch process utilizing the catalysts described herein is a slurry-type process wherein the catalyst having a fine particle size and a high surface area of above about 5 m²/g, preferably above 30 m²/g, is suspended in a liquid hydrocarbon and the carbon monoxide/hydrogen mixture forced through the catalyst slurry allowing good contact between the carbon monoxide/hydrogen and the catalyst to initiate and maintain the hydrocarbon synthesis process.

Advantages of a slurry process over that of a fixed bed process are that there is better control of the exothermic heat produced in the Fischer-Tropsch process during the reaction and that better control over catalyst activity maintenance by allowing continuous recycle, recovery, and rejuvenation procedures is implemented.

The slurry process can be operated in a batch or in a continuous cycle, and in the continuous cycle, the entire slurry can be circulated in the system allowing for better control of the primary products residence time in the reaction zone.

The slurry liquid used in the process is a liquid at the reaction temperature, must be chemically inert under the reaction conditions, must be a relatively good solvent for carbon monoxide/hydrogen and possess good slurrying and dispersing properties for the finely divided catalyst. Representative classes of organic liquids which can be utilized are high boiling paraffins, aromatic hydrocarbons, ethers, amines or mixtures thereof.

The high boiling paraffins include C₁₀-C₅₀ linear or branched paraffinic hydrocarbons; the aromatic hydrocarbons include C₂-C₂₀ single ring and multi and fused ring aromatic hydrocarbons; the ethers include aromatic ethers and substituted aromatic ethers where the ether oxygen is sterically hindered from being hydrogenated; the amines include long chain amines which can be primary, secondary and tertiary amines, wherein primary amines preferably contain at least a C₁₂ alkyl group in length, secondary amines preferably contain at least two alkyl groups being C₇ or greater in length, and tertiary amines preferably contain at least three alkyl groups being C₆ or greater in length.

The slurry liquid can contain N and O in the molecular structure but substantially no S, P, As or Sb, since these are poisons in the slurry process. Representative examples of specific liquid slurry solvents useful herein are dodecane, tetradecane, hexadecane, octadecane, cosane, tetracosane, octacosane, dotriacontane, hexatriacontane, tetracontane, tetracontane, tetratetracontane, toluene, o-, m- and p-xylene, mesitylenem, C₁-C₁₂ mono- and multi-alkyl substituted benzenes, dodecylbenzene, naphthalene, anthracene, biphenyl, diphenylether, dodecylamine, dinonylamine, trioctylamine, and the like. Preferred liquid hydrocarbon slurry solvents are octacosane and hexadecane.

The amount of catalyst used in the liquid hydrocarbon slurry solvent is generally about 10g to 60g of dry catalyst per 500g slurry liquid. Preferably about 30g to 50g dry catalyst per 500g slurry liquid slurry is utilized, being in about a respective 17:1 to 10:1 weight ratio.

The slurry system, comprised of the slurry liquid and finely divided catalyst, is generally stirred to promote good dispersion during the pretreatment in the process to avoid catalyst settling and to eliminate mass transfer limitations between the gas and liquid phases. In a typical laboratory unit the rate of stirring is generally carried out in the range of about 600 to 1,200 rpm and preferably 1,000 to 1,200 rpm.

Prior to the carbon monoxide/hydrogen hydrocarbon synthesis run, the copper promoted cobalt-manganese catalyst is generally conditioned in the apparatus by purging with nitrogen to remove reactive oxygen-containing gases and the temperature is increased while stirring to the reaction temperature range.

The carbon monoxide/hydrogen feedstream is then introduced into the slurry catalyst chamber and the pressure, space velocity, temperature, and hydrogen/carbon monoxide molar ratio is then adjusted, as desired for hydrocarbon synthesis conditions.

In the process, the hydrogen and carbon monoxide are preferably used in a molar ratio in the gaseous feedstream in about a 10:1 to 1:10 molar ratio, preferably 3:1 to 0.5:1, and in a particularly preferred molar ratio of 1:1 to 2:1.

The temperature in the process is generally in the range of about 200 to 300°C, preferably about 230 to 270°C and most preferably about 240° to 260°C. Higher temperature ranges can also be used but tend to lead to lighter products and more methane; lower temperature ranges can also be used but tend to lead to lower activity and increased wax formation.

The process is generally conducted at a pressure in the range of about 50 to 400 psig and preferably about 70 to 225 psig. Higher pressures can also be used but tend to lead to waxy materials, particularly in combination with lower temperatures.

The space velocity used in the process is generally about 100 to 4,000 volumes of gaseous feedstream/per volume of dry catalyst in the slurry/per hour and is preferably in the range of about 400 to 1,200 v/v/hr, and most preferably about of 800 to 1,200 v/v/hr. Higher space velocities can also be used but tend to lead to a lower rate of carbon monoxide conversion, and lower space velocities can also be used but tend to lead to more paraffinic products.

The extent of carbon monoxide conversion obtainable in the subject process, while providing substantial quantities of olefins, and higher paraffins, ranges from about 30% to 80% and usually about 30% to 60%.

"Total hydrocarbons" produced in the process is related to the selectivity of the rate of carbon monoxide conversion to C₁ to C₄₀ hydrocarbons. Total hydrocarbon selectivity is generally 50 to 90 percent and higher, of the total carbon monoxide converted, and the remainder converted to carbon dioxide.

The selectivity to methane based on the amount of carbon monoxide conversion is about 1 to 10 weight percent based on the total hydrocarbons produced. Preferably about 8 percent, or lower, methane is produced in the process.

As discussed above, the percent selectivity to carbon dioxide is about 10 to 50 percent of the carbon mon-

oxide converted.

Preferably, the reaction process variables are adjusted to minimize carbon dioxide production, minimize methane production, minimize percent carbon monoxide conversion, and minimize the selectivity of C_2 - C_{20} olefins and C_{5-30} paraffins while achieving activity maintenance in the catalyst system.

5 Generally, the preferred mode of operating the process includes using a highly paraffinic wax, such as octacosane as the slurry liquid, $Co_2MnO_4/1\%Cu$ as the catalyst, providing a catalyst/liquid weight ratio of about 8/72, stirring the system at about 1,200 rpm, and the process is conducted at a hydrogen:carbon monoxide molar ratio of about 2:1, a temperature of about 270°C, a pressure of about 75 psig, and a space velocity of about 2,000 v/v/hr. By carrying out the above process in the stated preferred variable ranges efficient activity
10 maintaining and production of preferred hydrocarbons can be achieved.

The effluent gases in the process exiting from the reactor may be recycled if desired to the reactor for further hydrocarbon synthesis.

The following Examples illustrate aspects of the invention.

15 Example 1 - Preparation of Catalyst

An aqueous solution was prepared containing 48.9g of $Co(NO_3)_2 \cdot 6H_2O$ and 24.1g of $Mn(NO_3)_2 \cdot 6H_2O$ in 125 ml water. This was added to an aqueous solution of 48.4g citric acid and 14.1 ml ethylene glycol in 25 ml water with stirring at 70-90°C. The mixture became thick after 1-2 hours, after which it was calcined in air at 350°C
20 for 30 minutes. X-ray diffraction analysis revealed an homogenous single phase spinel having the formula Co_2MnO_4 that was isostructural with Co_3O_4 . The spinel had a BET surface area of 30-60 m²/g.

A 12g sample of the resulting Co-Mn spinel was impregnated with copper by treating it with 0.46g $Cu(NO_3)_2 \cdot 6H_2O$ dissolved in water using the incipient wetness impregnation procedure. The material was then dried at 110°C.

25 The resulting catalyst composition had the empirical formula $Co_2MnO_4/1\%Cu$.

Example 2 - Use of Catalyst in Fischer-Tropsch Process

A copper promoted cobalt-manganese catalyst prepared as described in Example 1 was placed in a CSTR
30 (continuously stirred tank reactor) to be used as a slurry Fischer-Tropsch reactor. Prior to introduction of synthesis gas, the catalyst was reduced in situ by feeding a hydrogen/carbon monoxide gas into the reactor at a temperature of from 100 to 270°C, a space velocity of 1000 to 2000 v/v dry catalyst/hour, under a pressure of 75 psig, at a hydrogen concentration of 20-33% mol for 4 to 6 hours. The system was purged with nitrogen and then a Fischer-Tropsch reaction carried out using a synthesis gas feed of a 2:1 volume ratio of hydrogen to
35 carbon monoxide, the reaction conditions in the CSTR being adjusted to a temperature of 270°C, a pressure of 75 psig and a space velocity of 2000 v/v dry catalyst/hour. The reaction was carried out in octacosane solvent. The effluent gas from the reactor was monitored by an HP-5840A Refinery Gas Analyzer to determine the degree of CO conversion and the nature of the hydro- carbon products. The results are given in Table 1 below.

The Fischer-Tropsch reaction was repeated twice replacing the copper promoted cobalt-manganese catalysts with comparative cobalt-containing catalysts: (A) $Co_3O_4/1\%Cu$ and (B) Co_2MnO_4 . The results of the reaction are also given in Table 1.
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TABLE 1

5	<u>Example</u>	<u>1</u>	<u>1A(1)</u>	<u>1B(1)</u>
	Catalyst	$\text{Co}_2\text{MnO}_4/1\% \text{ Cu}$	$\text{Co}_3\text{O}_4/1\% \text{ Cu}$	Co_2MnO_4
	% Conversion	45	23	NIL
10	<u>Product Selectivity (wt%):</u>			
	CO_2	16	54	-(2)
	CH_4	7	40	-
	$\text{C}_2\text{-C}_4$	26	6	-
	C_5+	51	NIL	-
15	% Olefins in $\text{C}_2\text{-C}_4$	83	52	-

(1) Comparative Example

(2) Due to low conversion, it was not possible to detect meaningful levels of products

As can be seen from Table 1, the copper promoted cobalt-manganese catalyst of the present invention is significantly more active than the analogs with copper promotion but non manganese (1A), and with manganese but no copper promotion (1B).

Claims

- A catalyst composition comprising a copper promoted cobalt-manganese spinel, the spinel having the formula:

$$\text{Co}_{3-x}\text{Mn}_x\text{O}_4$$
 where x is from 0.5 to 1.2.
- A composition according to claim 1 wherein x is from about 0.7 to about 1.0.
- A composition according to claim 1 or claim 2, wherein the copper is present in an amount of from 0.1 to 5 gram atom percent based on the total gram atoms of cobalt and manganese in the dry composition.
- A composition according to any preceding claim, having a BET surface area of greater than 30 m²/g.
- A method for preparing a catalyst composition comprising a copper promoted cobalt-manganese spinel, the spinel having the formula $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ where x is from 0.5 to 1.2; which method comprises the steps of:
 - forming an aqueous solution containing (i) at least one cobalt and at least one manganese water-soluble salt and (ii) at least one alpha-hydroxy aliphatic carboxylic acid, the molar ratio of cobalt salt(s) to manganese salt(s) being at least 1.5:1;
 - evaporating the aqueous solution to yield a cobalt-manganese containing residue;
 - calcining the residue at elevated temperature for a time sufficient to produce the above-defined spinel, the spinel being substantially a single phase spinel that is substantially iso-structural with Co_3O_4 as determined by X-ray diffraction analysis; and
 - promoting, in known manner, the product from step (c) with copper.
- A method according to claim 5, wherein the alpha-hydroxy aliphatic carboxylic acid is selected from citric, glycolic, malic, glyceric, mandelic, tartaric and lactic acids, and mixtures thereof.
- A method according to claim 6, wherein the said acid is selected from citric and glycolic acid.
- A Fischer-Tropsch process for the conversion of a hydrogen/carbon monoxide synthesis gas to hydrocarbons by contacting the synthesis gas with a catalyst; characterised by employing the catalyst claimed in any of claims 1 to 4, in a reactor under Fischer-Tropsch conditions, the catalyst having first been reduced either ex situ of the reactor or in situ in the reactor.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92307115.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US - A - 3 907 716 (HAACKE) * Totality *	1-5	B 01 J 23/84 C 07 C 1/04
X	EP - A - 0 261 288 (EXXON RESEARCH AND ENGINEERING COMPANY) * Totality *	5-8	
A	-----	1-4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 J C 07 C 1/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 02-11-1992	Examiner TENGLER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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